Electronic Supplementary Information for

The making of ring currents

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Benzene

The trimerization of acetylene to benzene has been studied along an hypothetical concerted reaction pathway belonging to the D_{3h} symmetry point group. This can be conveniently described in terms of a Z-matrix, where the reaction coordinate (RC) is defined as the distance of the C≡C acetylene bonds to the center of symmetry, see below for an example.

```
X0
X12 X0   RC
X34 X0   RC   X12 a120
X56 X0   RC   X12 a120 X34 d180
C1  X12 CC2 X0   a90   X34 d0
C2  X12 CC2 X0   a90   X56 d0
H1  C1   CH   X12 HCC   X34 d180
H2  C2   CH   X12 HCC   X56 d180
C3  X34 CC2 X0   a90   X56 d0
C4  X34 CC2 X0   a90   X12 d0
H3  C3   CH   X34 HCC   X56 d180
H4  C4   CH   X34 HCC   X12 d180
C5  X56 CC2 X0   a90   X12 d0
C6  X56 CC2 X0   a90   X34 d0
H5  C5   CH   X56 HCC   X12 d180
H6  C6   CH   X56 HCC   X34 d180
Variables:
CC2          0.6787
CH           1.0788
HCC        125.3525
Constants:
RC           1.50
a120       120.0
a90         90.0
d180       180.0
d0           0.0
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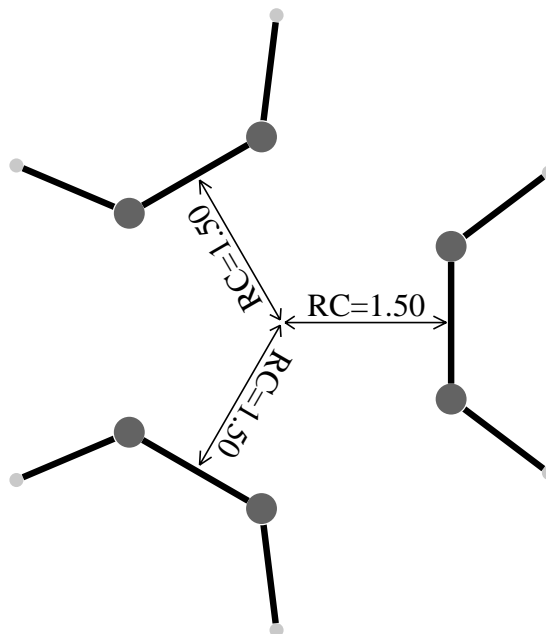
Distances are in Å and angles in degrees.

For each selected value of the reaction coordinate, only three geometrical parameters have to be optimized, i.e., the C-C and C-H bond lengths and the $\widehat{HCC}$ bond angle of the acetylene units. This has been done assuming a singlet closed-shell electronic configuration at the density functional theory (DFT) level of approximation, combining the B97-2 functional with the cc-pVTZ basis set and using the Gaussian 09 suite of programs. At this level of theory, the RC value for the D_{6h} benzene equilibrium geometry is 1.203 Å, which correspond to a C-C bond length of 1.389 Å. Reaction steps have been taken every 0.05 Å up to RC=2.00 Å, with a few finer exceptions.

Table 1: B97-2/cc-pVTZ optimized geometrical parameters and energies for the various steps of the hypothetical concerted trimerization of acetylene to benzene along the pathway of D_{3h} symmetry. RC is the reaction coordinate in Å; C≡C, C-H and $\widehat{HCC}$ are bond lengths (Å) and angle (degree) of the acetylene units; C $\cdots$ C is the length of the forming bond; E is the energy of the whole system in hartree. Equilibrium bond lengths and energy of acetylene at the same level of calculation are: C≡C=1.197 Å, C-H=1.062 Å, $E = -77.32865994\ E_h$.

RC	C≡C	C $\cdots$ C	C-H	$\widehat{HCC}$	E
1.203	1.389	1.389	1.081	120.0	-232.24566551
1.210	1.391	1.400	1.081	120.1	-232.24533772
1.250	1.398	1.466	1.080	120.7	-232.23375912
1.275	1.398	1.510	1.080	121.2	-232.21985345
1.300	1.394	1.555	1.080	121.7	-232.20235257
1.350	1.383	1.647	1.079	122.8	-232.16051294
1.400	1.370	1.740	1.079	124.0	-232.11411686
1.450	1.357	1.833	1.079	125.4	-232.06669953
1.500	1.343	1.926	1.078	127.0	-232.02060795
1.550	1.327	2.021	1.077	129.4	-231.97774425
1.600	1.303	2.120	1.075	133.3	-231.94038413
1.650	1.253	2.231	1.068	144.7	-231.91439711
1.700	1.213	2.338	1.059	157.3	-231.91144483
1.750	1.203	2.430	1.057	162.5	-231.91795249
1.800	1.198	2.519	1.055	165.9	-231.92667016
1.850	1.196	2.606	1.055	168.4	-231.93551626
1.900	1.195	2.693	1.055	170.5	-231.94366910
1.950	1.195	2.780	1.056	172.2	-231.95080309
2.000	1.195	2.867	1.056	173.6	-231.95688481

Figure 1: the animation shows the π electron first-order current density induced by a perpendicular magnetic field in points at 1 a_0 above the plane where the hypothetical $3C_2H_2 \rightarrow C_6H_6$ concerted reaction takes place. The modulus of the current density is proportional to the area of the plotted fat arrows with a fixed length/width ratio. The phase portrait of the current density vector field is also shown. Calculations have been performed using the continuous transformation of the origin of the current density (CTOCD-DZ2) method and the B97-2/cc-pVTZ combination of functional and basis set, as implemented in the SYSMO package. Singularities of the current density vector field are marked by green/red dots denoting diatropic/paratropic vortex centers and by blue crosses denoting saddle points. Black lines connect saddle points; these are trajectories of current density that represent the boundary of current domains. Current susceptibilities in nA T^{-1} are reported on the left for the forming C $\cdots$ C bonds and on the right for the C≡C acetylene bonds. Positive/negative values are relative to diatropic/paratropic current density cross sections.

Planar cyclooctatetraene (COT)

Similarly, the tetramerization of acetylene to planar cyclooctatetraene (COT) has been studied along an hypothetical concerted reaction pathway belonging to the D_{4h} symmetry point group. Also in this case, a Z-matrix can be written where the reaction coordinate (RC) is defined as the distance of the C≡C acetylene bonds to the center of symmetry.

```
X0
X12 X0   RC
X34 X0   RC   X12 a90
X56 X0   RC   X34 a90 X12 d180
X78 X0   RC   X56 a90 X34 d180
C1  X12 CC2 X0   a90 X34 d0
C2  X12 CC2 X0   a90 X78 d0
H1  C1  CH   X12 HCC X34 d180
H2  C2  CH   X12 HCC X78 d180
C3  X34 CC2 X0   a90 X12 d0
C4  X34 CC2 X0   a90 X56 d0
H3  C3  CH   X34 HCC X12 d180
H4  C4  CH   X34 HCC X56 d180
C5  X56 CC2 X0   a90 X34 d0
C6  X56 CC2 X0   a90 X78 d0
H5  C5  CH   X56 HCC X34 d180
H6  C6  CH   X56 HCC X78 d180
C7  X78 CC2 X0   a90 X56 d0
C8  X78 CC2 X0   a90 X12 d0
H7  C7  CH   X78 HCC X56 d180
H8  C8  CH   X78 HCC X12 d180
Variables:
CC2        0.69
CH         1.0817
HCC      117.1663
Constants:
RC         2.00
a90        90.0
d180      180.0
d0          0.0
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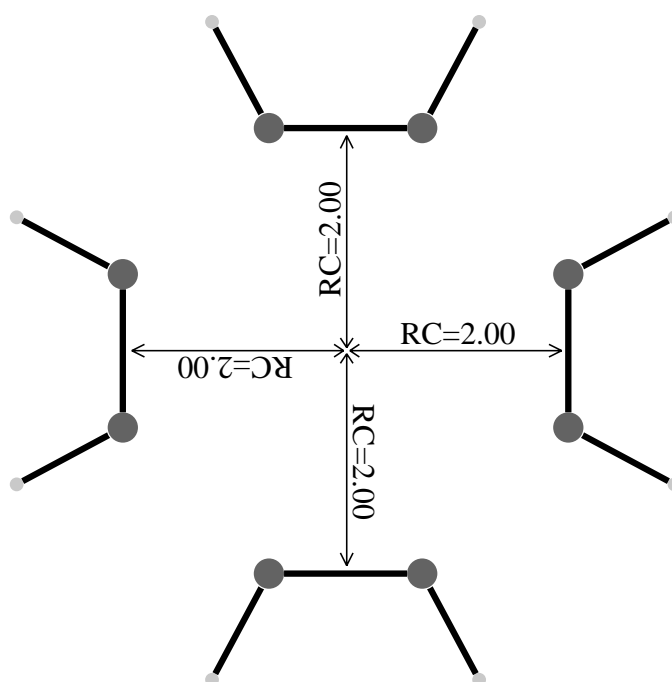

Distances are in Å and angles in degrees.

For each selected value of the reaction coordinate, the C-C and C-H bond lengths and the $\widehat{HCC}$ bond angle of the acetylene units have been optimized, with the same assumptions as in the previous case of benzene,. At this level of theory, the RC value for the planar D_{4h} COT equilibrium geometry is 1.708 Å, which correspond to a C=C double bond length of 1.338 Å and a C−C single bond length of 1.469 Å.

Table 2: B97-2/cc-pVTZ optimized geometrical parameters and energies for the various steps of the hypothetical concerted tetramerization of acetylene to planar COT along the pathway of D_{4h} symmetry. RC is the reaction coordinate in Å; C≡C, C-H and $\widehat{\text{HCC}}$ are bond lengths (Å) and angle (degree) of the acetylene units; C $\cdots$ C is the length of the forming bond; E is the energy of the whole system in hartree.

RC	C≡C	C $\cdots$ C	C-H	$\widehat{\text{HCC}}$	E
1.708	1.338	1.469	1.084	113.6	-309.56178796
1.710	1.339	1.471	1.084	113.7	-309.56176257
1.725	1.345	1.489	1.084	113.8	-309.56057609
1.750	1.353	1.518	1.083	114.1	-309.55494953
1.775	1.361	1.548	1.083	114.4	-309.54529048
1.790	1.365	1.566	1.083	114.6	-309.53779852
1.800	1.367	1.579	1.083	114.7	-309.53216935
1.850	1.376	1.643	1.082	115.4	-309.49761400
1.900	1.380	1.711	1.082	116.2	-309.45503647
1.950	1.380	1.782	1.082	117.2	-309.40757124
2.000	1.377	1.855	1.082	118.2	-309.35773673
2.050	1.371	1.930	1.082	119.3	-309.30747061
2.100	1.363	2.006	1.082	120.5	-309.25820335
2.150	1.354	2.083	1.082	121.9	-309.21096058
2.200	1.345	2.160	1.081	123.3	-309.16646523
2.250	1.335	2.238	1.081	125.0	-309.12521121
2.300	1.326	2.315	1.081	126.8	-309.08751635
2.350	1.316	2.393	1.081	128.8	-309.05354605
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
2.500	1.191	2.694	1.049	164.4	-309.21736548
2.600	1.191	2.835	1.050	168.0	-309.24257742

Figure 2: the animation shows the π electron first-order current density induced by a perpendicular magnetic field in points at 1 a_0 above the plane where the hypothetical $4C_2H_2 \rightarrow C_8H_8$ concerted reaction takes place. See the caption of the previous animation for other details.

Borazine

The simplest iminoborane, HBNH, is isoelectronic with acetylene, and an hypothetical concerted trimerization of HBNH to borazine can be devised along a reaction pathway belonging to the C_{3h} symmetry point group. As in the previous cases, a Z-matrix can be written where the reaction coordinate (RC) is defined as the distance of the B≡N iminoborane bonds to the center of symmetry, see below.

```
X0
X12 X0   RC
X34 X0   RC    X12 a120
X56 X0   RC    X12 a120 X34 d180
N1   X12 NX12 X0   a90   X34 d0
B2   X12 BX12 X0   a90   X56 d0
H1   N1   NH    X12 BNH   X34 d180
H2   B2   BH    X12 HBN   X56 d180
N3   X34 NX12 X0   a90   X56 d0
B4   X34 BX12 X0   a90   X12 d0
H3   N3   NH    X34 BNH   X56 d180
H4   B4   BH    X34 HBN   X12 d180
N5   X56 NX12 X0   a90   X12 d0
B6   X56 BX12 X0   a90   X34 d0
H5   N5   NH    X56 BNH   X12 d180
H6   B6   BH    X56 HBN   X34 d180
Variables:
BX12        0.7527
NX12        0.6572
BH          1.1874
NH          1.0031
HBN       129.3318
BNH       120.9993
Constants:
RC          1.60
a120       120.0
a90         90.0
d180       180.0
d0           0.0
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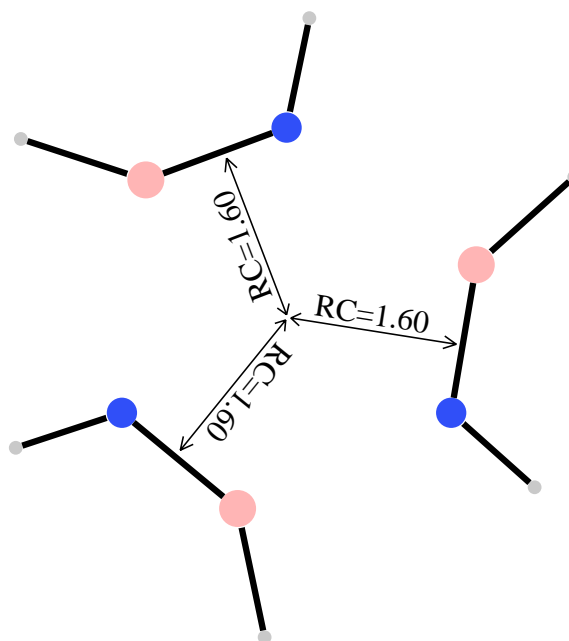
Distances are in Å and angles in degrees.

Owing to the lower symmetry with respect to benzene and planar COT, a few more geometrical parameters have been optimized, retaining the same assumptions as in the previous cases, for each selected value of the reaction coordinate. These are: the B≡N, B-H and N-H bond lengths and the $\widehat{\text{HBN}}$, $\widehat{\text{BNH}}$ bond angles of the iminoborane units. At this level of theory, the RC value for the D_{3h} borazine equilibrium geometry is 1.235 Å, which correspond to a B-N bond length of 1.428 Å.

Table 3: B97-2/cc-pVTZ optimized geometrical parameters and energies for the various steps of the hypothetical concerted trimerization of iminoborane to borazine along the pathway of C_{3h} symmetry. RC is the reaction coordinate in Å; B≡N, B-H, N-H, $\widehat{\text{HBN}}$ and $\widehat{\text{BNH}}$ are bond lengths (Å) and angle (degree) of the iminoborane units; B···N is the length of the forming bond; E is the energy of the whole system in hartree. Equilibrium bond lengths and energy of iminoborane (BH_2N) at the same level of calculation are: B-N=1.234 Å, B-H=1.170 Å, N-H=0.988 Å, $E = -80.80243798\ E_h$.

RC	B≡N	B···N	B-H	N-H	$\widehat{\text{HBN}}$	$\widehat{\text{BNH}}$	E
1.235	1.428	1.428	1.195	1.003	121.4	118.5	-242.66461636
1.250	1.433	1.450	1.195	1.003	121.7	118.8	-242.66359246
1.300	1.444	1.531	1.193	1.002	122.8	119.4	-242.64714263
1.350	1.441	1.619	1.191	1.002	124.4	120.1	-242.61689332
1.400	1.428	1.712	1.189	1.003	126.6	120.6	-242.57964930
1.450	1.410	1.808	1.187	1.003	129.3	121.0	-242.54039441
1.500	1.390	1.905	1.186	1.003	132.6	121.4	-242.50249637
1.550	1.369	2.003	1.184	1.004	136.6	121.7	-242.46820997
1.600	1.348	2.102	1.181	1.004	141.5	122.1	-242.43909250
1.650	1.327	2.201	1.178	1.004	147.1	123.3	-242.41617008
1.700	1.307	2.300	1.175	1.003	153.4	125.5	-242.39985122
1.750	1.288	2.400	1.172	1.000	159.8	129.7	-242.38980847
1.800	1.271	2.498	1.169	0.996	165.5	136.7	-242.38511489
1.850	1.257	2.595	1.168	0.992	169.8	145.1	-242.38438511
1.900	1.247	2.688	1.167	0.989	172.3	152.9	-242.38596352
1.950	1.241	2.781	1.167	0.988	174.1	159.3	-242.38855419

Figure 3: the animation shows the π electron first-order current density induced by a perpendicular magnetic field in points at 1 a_0 above the plane where the hypothetical $3\mathrm{BH_2N} \rightarrow \mathrm{B_3H_6N_3}$ concerted reaction takes place. See the caption of the previous animation for other details.
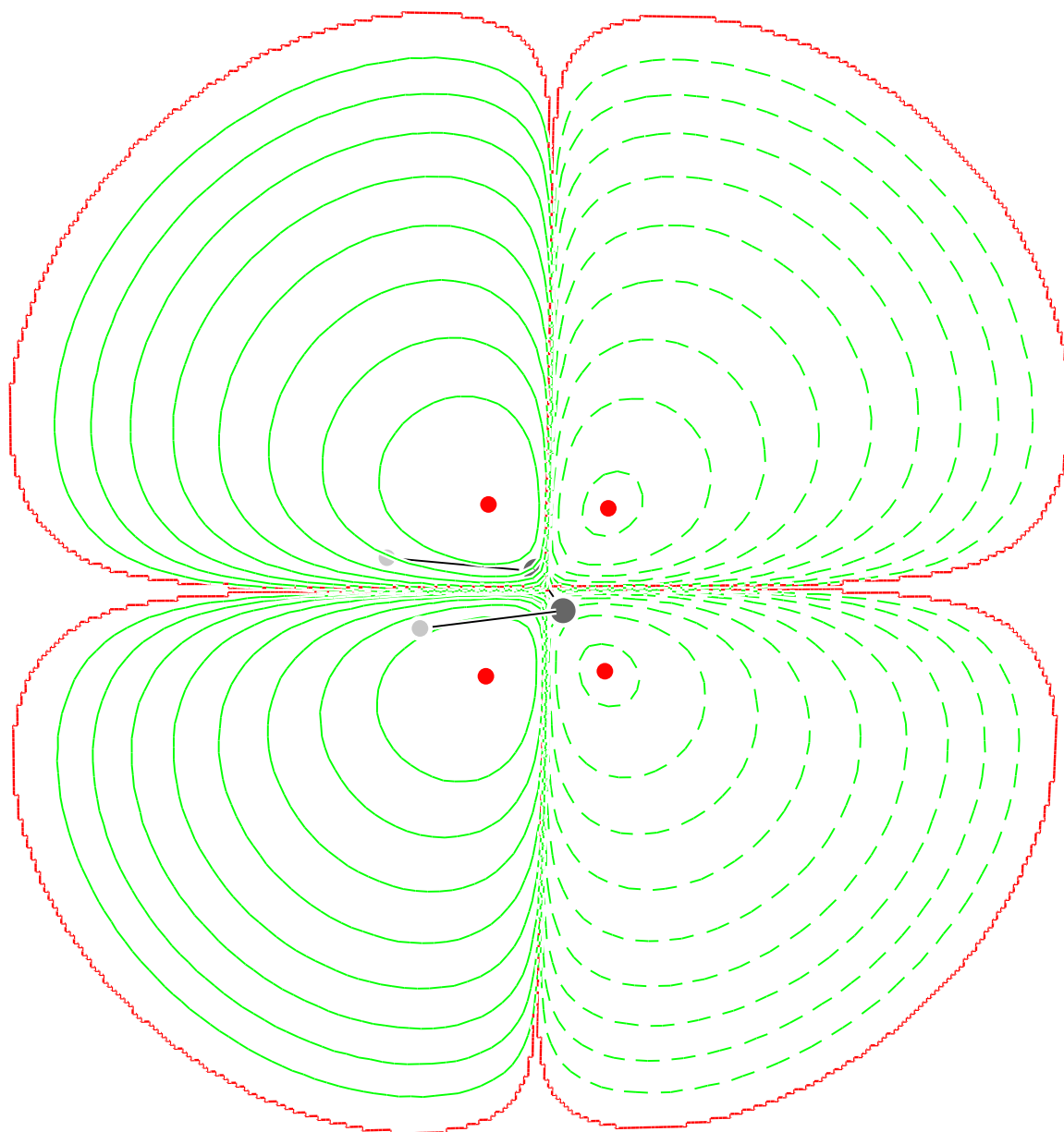
Figure 4: An example of the integration domains of the current density cross section for the calculation of the C≡C bond current strength of a distorted acetylene molecule. The inducing magnetic filed is perpendicular o the molecular plane.
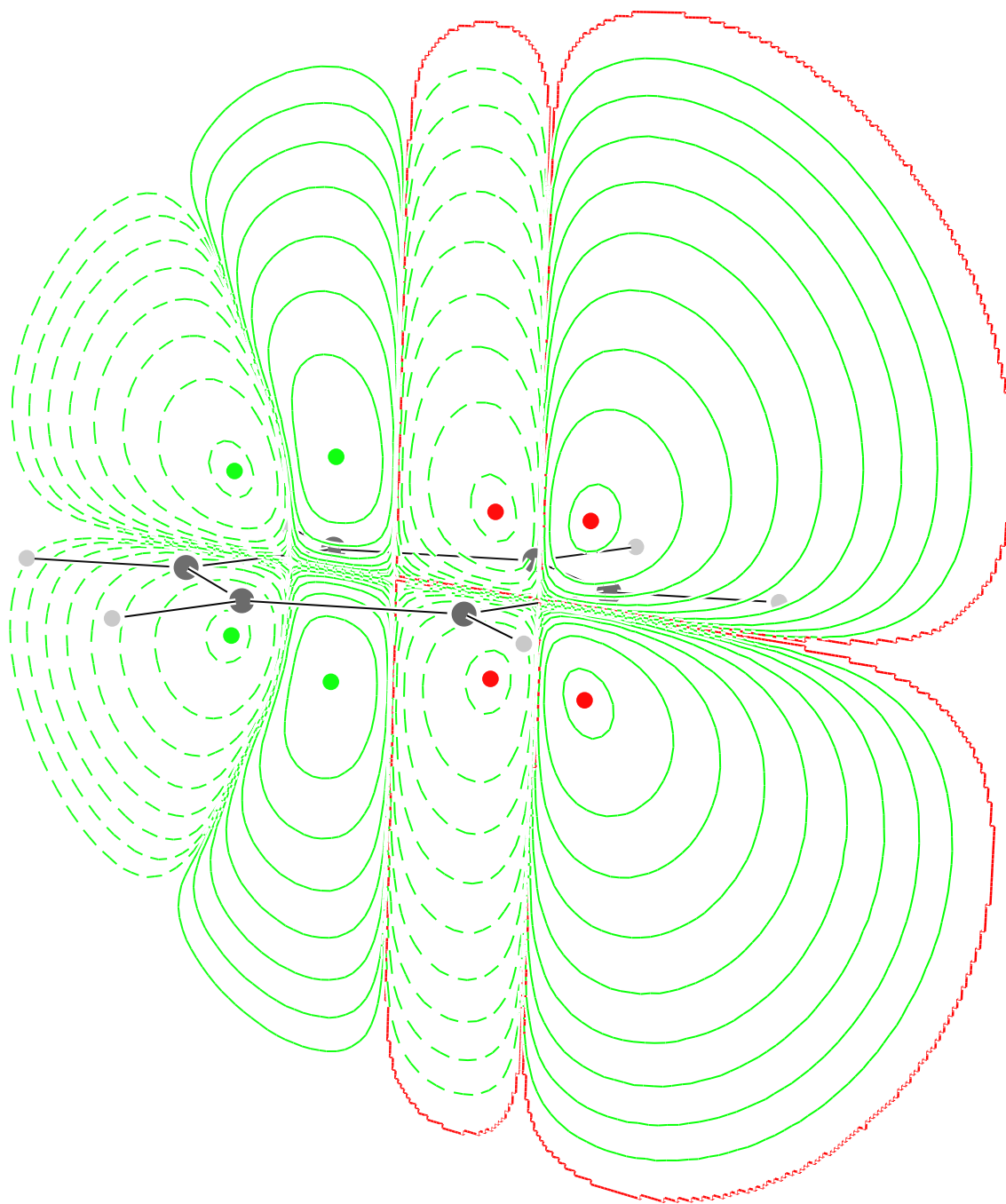
Figure 5: An example of the integration domains of the current density cross section for the calculation of the C≡C and C−C bond current strengths in one step of the trimrization of acetylene to benzene. The inducing magnetic filed is perpendicular o the molecular plane.